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The Oxidation Degradation of Aromatic Compounds

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## ABSTRACT

A series of experiments have been conducted which have focussed on understanding the role that O atom addition to aromatic rings plays in the oxidation of benzene and toluene. Flow reactor studies of the oxidation of toluene have given an indication of the amount of O atoms available during an oxidation and the degree to which O atom adds to the ring. Flow reactor studies of the oxidation of toluene and benzene to which NO<sub>2</sub> has been added, have shown that NO<sub>2</sub> appears to suppress the formation of O atoms and consequently reduce the amount of phenols and cresols formed by O atom addition. A high temperature pyrolysis study of phenol has confirmed that the major decomposition products are carbon monoxide and cyclopentadiene. A preliminary value for the overall decomposition rate constant has also been obtained.

## Introduction

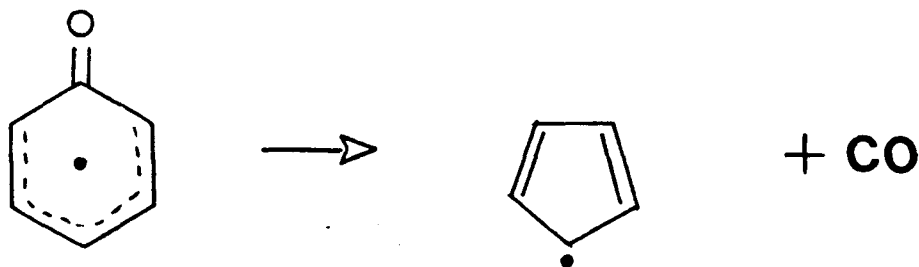
The realization that aromatics would be a major constituent in alternative fuels with significant attendant consequences (1) on soot formation and fuel stability has provided a practical impetus for detailed studies of the combustion chemistry of these species. Such detailed understanding is necessary for combustor modellers and to assist in unravelling reasons for the great sooting tendency of aromatic compounds. Chemical kinetic studies motivated by the need for increased detailed understanding have focussed either on single elementary reactions such as in molecular beam experiments (2,3) or on coupled reactions complicated by the diffusion of species and heat loss (4). Furthermore, temperatures in these studies have been either at room or flame temperatures. There is a middle ground in both chemical complexity and temperature that serves as the indispensable link between these extremes - the link provides an understanding of the intrinsic chemistry resulting from many coupled elementary reactions evolving in time, but free from the often unique and confusing influences of transport phenomena. It was the aim of this study to investigate some key aspects of the oxidation of benzene and toluene in order to help provide this essential missing link.

## Background

In a paper (5) based on the results of experiments on toluene and benzene oxidation in the Princeton University flow reactor, a mechanism for the oxidative degradation of the aromatic ring was outlined, Figure 1. This mechanism successfully explains the nature and sequence of intermediates formed in the oxidation process without requiring implausible radical-radical reactions or the formation of unstable peroxides. Also, the mechanism is one

of the first to give a clear view of the path by which the resilient aromatic ring fragments at temperatures less than 1800° K. The intermediate temperature range of 900-1200° K, and perhaps somewhat higher, for which this mechanism is important corresponds to the regime of initial chemistry in flames (6) and clearly makes the mechanism relevant to many high temperature combustion processes. Further it predicts the presence of vinyl acetylene and butadiene, as well as acetylene, as intermediates. These C<sub>4</sub>'s may be important precursors to soot.

A key feature of the mechanism is the breaking of the six carbon aromatic ring structures to produce a conjugated five carbon ring by the reaction



This reaction, the first in the series that leads to actual ring rupture is distinguished from postulated low temperature ring rupture steps (7) by the involvement of a single oxygen atom and not by a peroxide. The kinetics of phenoxyl radical decomposing unimolecularly to the cyclopentadienyl radical and carbon monoxide have been studied (8) and indicate that the reaction would be fast enough to continue the propagation of a chain mechanism (9) as the one we suggest in Figure 1.

The phenoxyl radical, the species crucially important in ring rupture, is postulated to be formed by the exothermic reaction of phenyl radical and molecular oxygen

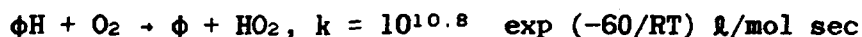


$$\Delta H = -11 \text{ kcal}$$

An estimation of the rate constant of this previously overlooked reaction by using the techniques of thermochemical kinetics (9) and empirical correlations (10) yields a lower bound rate constant at 1000 K of  $10^{9.2} \exp(-11.2/RT)$  l/mol sec (5). This rate constant also implies that the reaction is fast enough to sustain a chain reaction as the one suggested. In fact, after our recommendation of this possibility, the reaction of vibrationally hot phenyl radical and molecular oxygen was been investigated experimentally in another laboratory and the preliminary results indicate the reaction takes place quite readily (11).

Clearly, then, our postulated path to the oxidative ring rupture of aromatics is predicated on the existence of a phenyl radical and its subsequent reaction with molecular oxygen. When the hydrocarbon fuel is an aromatic ring with a side chain such as toluene or ethyl benzene, our previous experimental results have indicated that a phenyl radical will be produced by one of the major paths that first consumes the side chain (5). If the fuel is benzene, however, then the phenyl radical can be produced by a number of related ring hydrogen atom abstractions.

Early in the benzene reaction, when  $O_2$  is present in relatively large concentrations, phenyl radical will be formed by the abstraction reaction (12)



After the radical pool that is characteristic of high temperature combustion processes has built up, OH radicals and H and O atoms will be available for phenyl producing steps. It has been shown rather dramatically (13) that as the temperature of a OH/benzene system is increased from 300 K to = 1000 K a

change in the reaction mechanism occurs. At temperature  $< 500$  K the OH radical adds to the aromatic ring. At temperatures  $> 500$  K, OH will increasingly abstract H from the ring until a temperature is reached at which abstraction takes place to the complete exclusion of the addition reaction (13). This criterion of course implies that any OH in the combustion system at higher temperatures will react with benzene to form the important phenyl radical. H atoms react similarly with benzene to produce phenyl radicals or leave benzene essentially unchanged (14).

High temperature elementary reaction studies of benzene and toluene (15) have indicated that O atoms follow a quite different route than OH and H. Over the temperature range 300-1000 K, oxygen atoms have been found to add exclusively to the electron rich aromatic ring and not abstract hydrogen. The triplet adduct will rearrange to form phenol,  $C_6H_5OH$ , the path favored by higher collision energies and presumably higher temperature or will eliminate hydrogen atom to form phenoxy radical. From pyrolysis studies, phenol is known to decompose to cyclopentadiene and carbon monoxide (16):

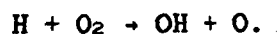


Evidently, the presence of oxygen atoms in an aromatic combustion system opens up the possibilities of alternative ring rupture paths. Oxygen atom reactions can lead to other chain reaction steps which would offer still another explanation for the presence of the intermediates phenol, cyclopentadiene, vinyl acetylene, butadiene etc. and their time histories as revealed by the flow reactor experiments. Evaluation of this oxygen atom effect was a key element of the proposed work.

A comparison of the rate constant for the reaction of oxygen atom and benzene,  $k = 10^{10.4} \exp(-4.9/RT)$  l/mole sec (15), with the estimated lower

bound rate constant for the reaction of molecular oxygen with phenyl radical,  $k = 10^{9.2} \exp(-11.2/RT)$  l/mol sec, might lead one to ask why it is even necessary to consider the much slower molecular oxygen/phenyl radical reaction as a ring rupture path. The answer to the question depends on the combustion environment considered. In a flame, oxygen atoms formed at the very hot flame front can diffuse upstream to meet unreacted fuel. A large concentration of oxygen atoms so formed would be expected to rapidly add to the aromatic ring; there is evidence that exactly this process occurs in premixed benzene flat flames (4). However, our goal was to examine the chemical aspects of the combustion process by eliminating, through experimental design, the influence of species transport on the chemistry and observing the manner in which many coupled elementary reactions develop in time. In this type of solely "kinetically evolving system", one that exists for the Princeton University flow reactor, it is not clear that an oxygen atom/benzene reaction would predominate.

In a kinetically evolving system the oxygen atom concentration may simply not be high enough for the atoms to appreciably react with benzene when the fuel concentration is high. It is characteristic of high temperature combustion systems (17) that oxygen atoms are primarily formed by the branching reaction



Since the overwhelming majority of H atoms available for the  $\text{H} + \text{O}_2$  reaction will come from the later steps of the ring rupture process, the availability of ring fragments at that time may be so high that any oxygen atoms produced in the branching reaction may react preferentially with the abundant olefinic, diolefinic or acetylenic fragments rather than with the benzene.

There are other points to consider when evaluating the oxygen atom/benzene reaction as an alternative to the degradative route of the molecular oxygen/phenyl radical reaction. There is considerable evidence that suggests that phenol will be the major addition product of oxygen atom reaction with benzene (2,3,4,18,19). Cypres and Bettens (16) have indicated that phenol will decompose to carbon monoxide and cyclopentadiene, but they did not measure the rate constant. Such a decomposition would explain the observation of a number of researchers of the formation of carbon monoxide in an oxygen atom/benzene system (2,18). Other experiments, however, have not yielded carbon monoxide as a reaction product leading researchers to suggest that the carbon monoxide observed by some is either the result of secondary reactions or experimental artifact (3,15). The essential point here is that even if oxygen atoms are abundant enough to add to the aromatic ring, the phenolic product may decompose at a very slow rate - a rate so slow that the decomposition reaction of phenol cannot be a major route to ring rupture in aromatics combustion.

The last reservation to consider is that, with the exception of the Nicovich, Gump, Ravishankara (15) study, all the experiments examining the single oxygen atom/benzene reactions have been at room or low ( $< 500$  K) temperature. Even though the high temperature study of the Georgia Tech group has yielded very important results, it was limited because only reactant disappearance was monitored quantitatively and a search for only the carbon monoxide product was made. There is considerable evidence now for the non-Arrhenius behavior of reactions at high temperatures (20) and even for changeovers in reaction mechanism (13). Furthermore, it is known that



depending on the location of the energy barrier along the reaction coordinate (21). In some cases arguments for the location of the energy barrier based on experimental evidence, such as those made by Sibener, et al. (3) for example, can be helpful in deducing temperature effects. Nevertheless, a cogent argument can be made for conducting complementary experiments in which both reactant and product histories are examined over the high temperature range of ultimate interest.

The preceding discussion has focussed on a classic situation in which two reaction paths, phenyl radical/molecular oxygen and atomic oxygen/benzene, are viable alternative explanations for the same observed phenomenon of aromatic ring destruction. The phenyl radical/molecular oxygen path is self consistent and quite plausible in all respects. Furthermore, it is currently being experimentally confirmed (11). The atomic oxygen/benzene path is also quite possible, but as outlined in detail in the preceding paragraphs a number of questions are associated with it. The existence of these two reaction alternatives creates an ambiguity in understanding the combustion chemistry of aromatics - an ambiguity that we proposed to experimentally resolve by addressing directly the questions surrounding the atomic oxygen/benzene degradation route.

### Experimental

The central piece of apparatus in our study of aromatics oxidation has been the Princeton University turbulent flow reactor. The experiments performed required further use of the flow reactor. Consequently, a brief description of the apparatus is appropriate. More detailed descriptions are available in the literature (22).

A schematic of the flow reactor is shown in Figure 2. Reaction temperature is achieved by preheating approximately 15% of the total nitrogen carrier gas flow in a plasma arc torch and then diluting with a much larger amount of cool nitrogen in the inlet section to produce a carrier gas stream at about 1000° K. Various temperature control mechanisms allow an effective operating range of roughly 900–1200° K. Oxygen is added to the hot carrier gas in the inlet section. In a lower pressure venturi region, fuel is added through four opposed injection tubes. Rapid mixing occurs and reaction begins. The reactants and developing products are then swept downstream through the reaction tube.

Gas flows are chosen so that flow in the reaction tube is turbulent. Therefore, radial homogeneity of mass flow, temperature and composition (plug flow) is achieved. Since fuel is introduced in very small quantities, typically much less than one mole percent, the reacting system is maintained at essentially constant volume conditions. Dilute conditions also minimize longitudinal diffusion. Heat loss is minimized and insures adiabatic operation. Once a carrier gas flow velocity is chosen that will place the desired extent of reaction in the reaction tube, a constant mass fuel rate establishes steady state operation.

As a result of this careful selection of operating conditions, samples withdrawn from a position in the flow reactor will be identical in composition to samples withdrawn from a well stirred constant volume batch reactor with the same time history (23). A series of experiments have confirmed the complementary nature of flow reactor data (24,25). The tremendous advantage of a flow reactor, though, results from the transformation of the time domain coordinate of a batch reactor to the position domain coordinate of the flow

reactor. Under conditions of steady state operation, a probe can withdraw samples for literally hours at a position in the flow reactor that corresponds to an elapsed time of milliseconds in a batch reactor. Consequently, very fast oxidation reactions or reactions with low conversion rates such as pyrolyses can be very effectively studied in the flow reactor. Since conditions are optimized to prevent products from later extent of reaction from diffusing upstream, the chemistry of this kinetically evolving system can be studied without interference from the diffusive transport of species.

Typical results from flow reactor oxidation studies are plotted against an abscissa which is labeled either as distance from injection or relative reaction time. The ordinate is normally the mole fraction percent of species at each of 15 discrete positions in the flow reactor. Samples are generally identified by gas chromatography-mass spectrometry and quantitatively measured by gas chromatography. The integrity of samples is maintained by the use of a highly developed gas sampling train (26). The basic components are a water-cooled quench probe maintained at 70° C, a heated transfer line and 16-position heated gas sampling valve that can be interfaced to and operated automatically by a microprocessor-controlled gas chromatograph. Note that this sampling system allows for identification and quantification of only stable species. The presence of radicals in a reaction sequence must be inferred from the presence of the stable species that they would produce. An optical system for the in situ measurement of OH radicals is currently being developed as part of another program.

## Results and Discussion

### A) Oxidation of Toluene

A series of toluene oxidation experiments were conducted both to examine the amount of cresols that would be formed through O atom addition to the aromatic ring and also to form a data base for further experiments in which the O atom concentration was perturbed. A set of species profiles from a lean oxidation experiment ( $\phi = 0.63$ ) is shown in Figures 3 and 4 and the data from a rich oxidation experiment ( $\phi = 1.4$ ) are shown in Figures 5 and 6.

From the concentrations of cresols present it was possible to estimate the concentration of O atoms that had added to the toluene. The calculation is based on the fact that Nicovich, Gump, and Ravishankara (15) have shown that up to temperatures of ca. 1000 K oxygen atoms add exclusively to the aromatic ring of toluene presumably to form primarily cresols. Therefore the concentration of oxygen atoms can be calculated by using the available rate constant for addition, the rate expression for cresol formation

$$\frac{d(\text{cresol})}{dt} = k[\phi\text{CH}_3][\text{OH}]$$

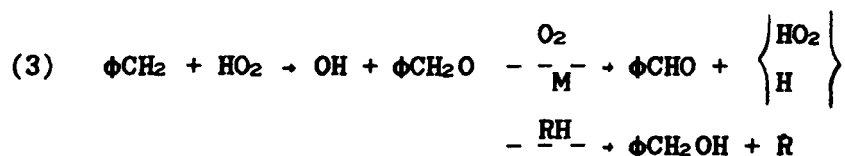
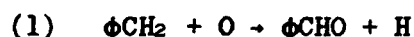
and experimental values for  $d(\text{cresol})/dt$  and toluene concentration determined from the slope of the cresol concentration plots. Because cresol decay paths are neglected, other O atom addition products are ignored, and the observed toluene concentration overestimates the available toluene due to the fact that benzyl radicals will also be observed as toluene, the rate equation will yield a lower-bound oxygen atom concentration.

Figures 4 and 6 display the total concentration of ortho, meta, and para cresol formed in the lean and rich oxidations of toluene. Using the rate constant  $k = 2.56 \times 10^{10} \exp(-3800/RT) \text{ l/mol s}$  (17),  $d(\text{cresol})/dt = 1 \times 10^{-3} \text{ mol fraction/s}$  and  $4 \times 10^{-4}$  obtained from the growth of cresol concentration at 11 and 21 ns and toluene concentrations of  $1.22 \times 10^{-3}$  and  $1.36 \times 10^{-3} \text{ mol}$

fraction at these times the lean and rich O atom concentrations of  $1.4 \times 10^{-8}$  and  $5.0 \times 10^{-9}$  mol fraction, respectively, were calculated.

Once this conservative estimate of the oxygen atom concentration was made, it was possible to address the important issue of how the benzyl radicals formed from the initial fuel were consumed during oxidation.

Though the evidence suggests that benzyl radical disappears during flow reactor toluene oxidation experiments by a route forming benzaldehyde, the mechanism by which the benzaldehyde is formed is still unresolved. In a mechanism suggested previously (5) the elementary step  $\phi\text{CH}_2 + \text{O}_2 \rightarrow \phi\text{CH}_2\text{O} + \text{O}$  followed by  $\phi\text{CH}_2\text{O} \rightarrow \phi\text{CHO} + \text{H}$  was presented as a rationale for the observed concentration time profile of benzaldehyde formation. However, as will be confirmed shortly, the slow rate of the first step would prohibit this route from being the primary source of benzaldehyde. Based on an extensive model for methane oxidation (27,28), methyl radical reactions shown to be important for the formation of formaldehyde may have the following benzyl radical counterparts leading to benzaldehyde and other related species:



All of the above postulated steps involve the reaction of a radical or atom with the benzyl radical, which is primarily formed by abstraction of an H by OH (13) but also pyrolytically from toluene (29). Ordinarily, radical-radical or radical-atom reactions are not important in the mechanisms of high-temperature combustion systems because other more rapid reactions occur first,

and often involve either an initial reactant still present in high concentration or an abundant stable intermediate. One of the most common competitive radical reactions occurring in hydrocarbon oxidation at flow reactor temperatures is the abstraction of a hydrogen from the carbon adjacent to the radical site by molecular oxygen to form an olefin (30). Since for the benzyl radical there is no adjacent abstractable hydrogen, an olefin forming path is simply not available.

An indication of the propensity of benzyl radical to build up in concentration and undergo radical-radical reactions is the amount of dibenzyl formed through benzyl self-association. In Figures 3 and 5, the dibenzyl concentration profile is plotted for both the lean and rich toluene oxidation conditions. Comparing the scale in Figures 3 and 5 with those in Figures 4 and 6 where the important oxygenated intermediates are plotted, one finds that the dibenzyl concentrations are of the same order of magnitude as these intermediates.

An additional measure of the relative importance of benzyl radical-radical (atom) reactions is the ratio of the rate of one of the most likely radical-atom benzaldehyde forming reactions to the rate of the most likely nonradical-radical (atom) routes to benzaldehyde

$$\begin{aligned} \frac{\text{rate of benzyl} + \text{O atom}}{\text{rate of benzyl} + \text{molecular oxygen}} &= \frac{k_1 [+CH_2] [O]}{k_6 [+CH_2] [O_2]} \\ &= \frac{k_1 [O]}{k_6 [O_2]} \end{aligned}$$

The ratio can be evaluated for reasonable estimates of  $k_1$ ,  $k_6$ , and a measured  $O_2$  concentration and by taking advantage of the occurrence of an oxygen atom - aromatic ring reaction, one of the few to occur before side chain oxidation is complete, to indicate quantitatively the concentration of oxygen atoms present early in the reaction sequence.

Introducing these oxygen concentrations, the measured lean and rich  $O_2$  concentrations of 2.17% and 0.88%, the values of  $10^{10.2}$  L/mol s for the benzyl radical-atomic oxygen association rate constant,  $k_1$ , and  $10^{9.8} \exp(-43000/RT)$  for the benzyl radical/molecular oxygen metathesis rate constant,  $k_6$ , lean and rich ratios of  $10^{2.2}$  and  $10^{2.1}$  are obtained. Clearly, the radical-atom association reaction is favored even under fuel rich conditions. To the extent that the actual O atom concentration is even larger than the lower-bound concentration estimated, the rate of the benzyl plus atomic oxygen reaction will be increased and favored even more so.

The conclusions that can be drawn from the detailed examination of the oxidation of toluene are 1) at temperatures around 1000 K, at atmospheric pressure, and in the absence of species diffusion, the reactions of benzyl radicals with radicals and atoms are unusually important in the formation of intermediate species. The association reactions of benzyl radicals with hydroperoxyl radicals and oxygen atoms are the primary sources of the benzaldehyde formed during toluene oxidation. Under these same conditions, the reaction of the benzyl radical with molecular oxygen is not an important source of benzaldehyde. The association reaction of the benzyl radical with OH is responsible for the benzyl alcohol observed. It is expected that subsequent reactions of benzyl alcohol with radicals also will contribute in part to the formation of benzaldehyde. It should be noted that at high temperatures, for example those of flames, the relative significance of these reactions could change. One quite obvious influence of higher temperatures would be a decrease in the concentration of hydroperoxyl radical formed by the reaction  $H + O_2 + M \rightarrow HO_2 + M$  because of the negative activation energy this reaction possesses (31). A decrease in hydroperoxyl concentration would serve

to further increase the importance of the benzyl radical association reaction with atomic oxygen; 2) toluene oxidation may be unrepresentative of the oxidation of longer chain n-alkylated aromatics at flow reactor temperatures just as methane oxidation is unrepresentative of the general mechanism of alkane oxidation. This fact appears to be true for very much the same structural reasons in each case: the absence of a hydrogen. However, only experimental studies of the oxidation of other n-alkylated aromatics such as ethylbenzene and n-propyl benzene can confirm this supposition. Note that certain high-temperature experiments such as soot formation measurements in flames do not detect a difference in effect between the various alkylated aromatics since the controlling factors are unrelated to the mechanism of side chain oxidation (32); 3) Though the benzyl radical is formed very easily and some eventually becomes a dibenzyl dimer during toluene oxidation, the absence of stilbene under both lean and rich conditions suggests that dibenzyl formation does not provide an alternative degradation path as ethane formation does during methane oxidation (33).

#### B) The Addition of $\text{NO}_2$ to the Oxidation of Toluene

Once the toluene experiments had been completed, a series of flow reactor experiments were begun which involved the addition of  $\text{NO}_2$  to the oxidations of toluene already examined. The addition of  $\text{NO}_2$  to a well characterized toluene oxidation experiment is the essence of the program to perturb the O atom concentration during the oxidation of toluene and benzene and thereby evaluate the importance of O atom addition reactions.

Nitrogen dioxide was added to a Princeton flow reactor (34) toluene oxidation experiment in concentrations of  $3 \times 10^{-5}$  and  $1.8 \times 10^{-4}$  mole fraction in two different studies. A comparison of selected species profiles



from the toluene oxidation without  $\text{NO}_2$  and with  $1.8 \times 10^{-4}$  mole fraction  $\text{NO}_2$  added is shown in Figure 7a,b. Before any detailed examination of the effect of  $\text{NO}_2$  on toluene oxidation can be attempted from the results in Figure 1, a measure of the precision of flow reactor data is necessary.

In Figures 8a,b are displayed data from two different toluene oxidation experiments conducted on different days but at the same initial conditions. From Figure 8 it can be seen that reproducibility is excellent for the species toluene, benzaldehyde, benzyl alcohol and benzaldehyde. Reproducibility of the measurements of phenol and cresol is not quite as good and is characteristic of these highly polar compounds. Similar levels of precision as those in Figure 8 are found with the species profiles obtained from the toluene oxidation experiments with  $\text{NO}_2$  added.

By examining Figure 7, with the results of Figure 8 kept in mind as a measure of precision, it can be seen that quite large effects result from the addition of  $1.8 \times 10^{-4}$  mole fraction of  $\text{NO}_2$ . The concentration of toluene is greatly decreased by the presence of  $\text{NO}_2$  during the entire residence time. The concentration of both benzaldehyde and benzene is increased by the presence of  $\text{NO}_2$  but the effect decreases with time. The greatest effect of adding  $\text{NO}_2$ , however, seems to be the almost complete inhibition of the formation of phenol and the cresols. Only at the very end of the residence time in the flow reactor is there an indication that phenol may be returning to its uninhibited levels. Similar but smaller effects as these were observed when only  $3 \times 10^{-5}$  mole fraction of  $\text{NO}_2$  was added to a toluene oxidation.

In a recently published paper on toluene oxidation (34) and in the above discussion of toluene oxidation, it was shown that reactions deduced by analogy with reactions occurring in the mechanism of methane oxidation can be

used to explain the appearance of benzaldehyde and benzyl alcohol during toluene oxidation. By following the same reasoning, reactions developed by analogy with those important in methane,  $O_2$ ,  $NO_2$  systems can be expected to be important in understanding the toluene,  $O_2$ ,  $NO_2$  flow reactor results.

A number of shock tube studies of the effect of  $NO_2$  on methane/ $O_2$  ignition characteristics have been conducted (35,36,37,38). A comprehensive study published by Slack and Grillo (39) provided a mechanism for the interaction of  $NO_2$ ,  $CH_4$  and  $O_2$  that not only explained their own results but also those of previous studies by other researchers. The mechanistic conclusions of Slack and Grillo (39) are therefore the ones that have been used as the basis for the following steps suggested to be important in the  $\phi CH_3$ ,  $O_2$ ,  $NO_2$  system:

- a.  $\phi CH_3 + OH \rightarrow \phi CH_2 + H_2O$       fuel consumption
- b.  $\phi CH_2 + NO_2 \rightarrow \phi CH_2O + NO$
- c.  $\phi CH_2 + M \rightarrow \phi CHO + H + M$       benzaldehyde formation
- d.  $H + NO_2 \rightarrow OH + NO$       radical regeneration

Notice that  $O_2$  is not directly involved in any steps of the above scheme, not even through the usually important step  $H + O_2 \rightarrow OH + O$ . Instead, the much faster reaction of  $H$  with  $NO_2$  is included. Even when the large  $O_2$  concentration is taken into account, the rate of reaction d is still approximately 10 times faster than the rate of  $H + O_2$ . As a result,  $NO$  is produced at the expense of  $O$  and the concentration of  $O$  atoms is expected to be less than  $10^{-7}$  mole fraction the approximate amount of  $O$  atoms present during a toluene oxidation without  $NO_2$  (34). In addition to the expected decrease of  $O$  atoms due to the  $H + NO_2$  reaction another route to the depletion of  $O$  atoms has been pointed out. The reaction of  $O$  with  $NO_2$  to form  $O_2$  and  $NO$

has been found to severely deplete O atom concentrations during the oxidation of methane in the presence of NO<sub>2</sub> (35). Together, then, the reactions  $H + NO_2$  and  $O + NO_2$  serve to greatly reduce the O atom concentration during the oxidation process.

One of the goals of this research was to perturb the O atom concentration and through observation of the effect of the perturbation on products deduce mechanistic information. The addition of NO<sub>2</sub> seems to lead to this type of large perturbation in the O atom concentration. If this perturbation in fact exists, then it seems that the large reduction in the amount of phenol and cresols produced during toluene oxidation is related to the reduction in O atom concentration. One explanation for this effect is that under NO<sub>2</sub> free conditions the phenol and cresols that are observed have been formed through O atom addition to benzene and toluene respectively. The reduction in O atom concentration resulting from the presence of NO<sub>2</sub> essentially stops the O atoms addition reactions.

As the previous discussion in this report has shown, cresol formation is a measure of O atom addition to toluene. The inhibition of cresol formation by NO<sub>2</sub> is therefore not surprising. However, the possibility that all the phenol observed is not actually phenoxy that has formed phenol on probe sampling, but is instead phenol formed directly through O atom addition to benzene makes it necessary to examine the suggestion that phenyl radical reacts with O<sub>2</sub> to form phenoxy and O is important during the oxidation of toluene and benzene (5).

Besides reducing the phenol and cresol concentrations, the presence of NO<sub>2</sub> greatly increases the benzaldehyde and benzene concentrations. Though it has been shown that benzaldehyde formation in NO<sub>2</sub> free systems is primarily

the result of O atom and HO<sub>2</sub> reactions with benzyl radical (34), the expected reduction in O atom concentration is offset by the alternative benzaldehyde formation paths 2 and 3. Benzene (or phenyl radical) is generally produced from benzaldehyde so that an increase in benzaldehyde concentration would lead to the type of benzene concentration increase observed.

It is also interesting to note that the steps a,b,c and d do not account for the benzyl alcohol observed. It has been shown (34) that the radical-radical reaction of OH with benzyl is the source of benzyl alcohol formed during the oxidation of toluene. It is expected that this same reaction produces benzyl alcohol when NO<sub>2</sub> is present. If this reaction proceeds, then the fact that the benzyl alcohol profile is essentially unchanged when NO<sub>2</sub> is added to the toluene oxidation implies that the product  $[\phi\text{CH}_2][\text{OH}]$  is also unchanged. This conclusion is difficult to reconcile with the observed decay of toluene.

#### C) The Addition of NO<sub>2</sub> to the Oxidation of Benzene

Since one of the primary areas of research interest under this program has been understanding the reactions of O atom and benzene, a series of preliminary experiments examining the effect of NO<sub>2</sub> on a stoichiometric benzene oxidation were performed. The results of these flow reactor studies are given in Figures 9 and 10. These figures clearly demonstrate the accelerative effect that the addition of NO<sub>2</sub> has on the rate of benzene decay. Concomitant with the accelerated benzene consumption is a suppressed rate of phenol and cyclopentadiene formation and an increased rate of vinyl acetylene and butadiene growth. Though these are fascinating observations, they are very difficult to reconcile with each other. A mechanism that describes the accelerative effect of NO<sub>2</sub> on benzene could be formulated, but one that is

also consistent with a decrease in both phenol and cyclopentadiene and an increase in C<sub>4</sub> species is still not yet available. Further experimentation would be necessary in order to clarify these observations.

#### D) The Pyrolysis of Phenol

The arguments outlined in this report have suggested that phenol may be formed as a major product in the O-atom addition to the benzene ring. However, in systems where the phenyl radical is produced, molecular oxygen may react directly with the phenyl radical to form phenoxy radical and O atom. At sufficiently high temperatures, both of these products are thought to decompose to CO and a five-carbon compound, and thus provide alternate ring rupture paths during the benzene oxidation process. In order to determine the relative importance of the reactions of benzene with O and phenyl with molecular oxygen as routes to ring rupture, an examination of phenol pyrolysis, with the determination of a rate constant for the decomposition, was initiated. Additionally, identification and quantification of phenol pyrolysis products were attempted in order to provide further information on whether the major portion of the phenol decays or returns to benzene, and the mechanisms associated with each route.

In these experiments, the reactant consisted of different weights of phenol crystals (99% pure) dissolved in benzene. As a fuel, this liquid mixture has several advantages over pure phenol. First, the benzene acts as a convenient carrier for the phenol crystals and does not itself decompose at the temperatures reached in this study (40) (see Figure 11). In addition, the presence of both benzene and phenol in the flow reactor partially simulates conditions encountered in benzene oxidation studies. There is one major drawback. As will be shown later, the large concentrations of benzene present

from the reactant carrier gas obscure some of the benzene formed from the phenol decomposition and hence interfere with proper quantification of the pyrolysis pathways.

Phenol pyrolysis studies were conducted at 1 atm pressure and 901° C, with initial reactant concentrations varying from 0.075 to 0.168 mole % phenol. The slope of the phenol decomposition curve for each initial concentration was calculated using a linear least squares fit to all 15 data points. The order with respect to concentration or true order,  $n$ , of the decomposition was taken from the slope of a plot of the initial decay rate and initial concentration (41):

$$\ln \frac{d(C_{\text{phenol}})_i}{dt} = \ln k + n \ln [C_{\text{phenol}}]_i$$

and the constant,  $k$ , for phenol pyrolysis at 1 atm and 901° C was obtained from the intercept.

A plot of  $\ln [d(C_{\text{phenol}})_i/dt]$  versus  $\ln [C_{\text{phenol}}]_i$  is shown in Figure 12. From the figure, it can be seen that phenol follows an approximately 1st order decomposition route with  $n = 0.94$  and  $k$  at 901°C and 1 atm = 2.0 sec<sup>-1</sup>. Table 1 shows that when the rate constant value of 2.0 sec<sup>-1</sup> is used with the integrated expression for first order decay of fuel, the fraction of fuel consumed is quite adequately predicted at a variety of extent of reaction. The table also shows that during the approximate 125 msec of residence time in the flow reactor nearly 20% of the phenol is decomposed. However, for reactor temperatures below 895°C and the same initial reactant concentrations, no phenol decay was observed. The result suggest that 895°C may be a minimum temperature for which phenol decay is important on time scales encountered in the flow reactor.

Figures 13a,b,c show species concentration profiles for a pyrolysis experiment using 0.097 mole% phenol as reactant, and Figure 13d, illustrates minor species concentrations in pyrolysis using 0.147 mole% phenol. Plots of product distribution from experiments with differing initial phenol concentrations give similarly shaped profiles for all species. These indicate that at 910°C, phenol does undergo some ring rupture within the flow reactor time scale and therefore could provide an important alternative ring rupture pathway in benzene oxidation systems.

One of the major paths of phenol decomposition is through the formation of CO and cyclopentadiene (16). If all the phenol decayed along this route, the rate of disappearance of phenol should equal the rate of increase in CO and cyclopentadiene. In the present studies, however, only about 60% of the phenol decay is accounted for by CO formation (Figure 13a,b). This result is in good agreement with the 65% previously reported (16). Additionally, the rate of CO formation is approximately 1.9 times greater than that of cyclopentadiene (Figure 13b), and indicates that perhaps pyrolysis of  $C_5H_6$  is occurring simultaneously at these temperatures or that there is another source of CO. The distribution of product species concentration (Figure 13c) indicate that cyclopentadiene decomposes to  $CH_4$ ,  $C_2H_2$  and  $C_2H_4$ ; however, all of the difference between CO and cyclopentadiene concentrations cannot be explained by these 3 products. Several investigators (42,43,44) have indicated that in addition to the 3 products mentioned, large amounts of benzene form during cyclopentadiene pyrolysis. In the present experimental system however, due to the large concentrations of benzene already present from the phenol carrier gas, small increases in benzene concentration will go unnoticed and the possibility of benzene formation exists.

In addition to  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_4$ , many minor decomposition products (<1.5 ppm) were identified using the GC/MS system (Figure 13d). Among these are vinylacetylene, methylacetylene, and propylene (see also ref. 42), allene, butadiene, several open ring  $\text{C}_5\text{H}_6$  compounds, phenylacetylene, styrene, toluene and indene (see also Ref. 43). There is the possibility that a small portion of cyclopentadiene builds to tetraline and appears as indene according to mechanisms outlined by Cypres and Bittens (44). One source of the discrepancy between CO and cyclopentadiene formation rates can be explained by a product that cannot be observed in the present system.

Similar to the phenomena noted with regard to cyclopentadiene pyrolysis, the total rate of phenol disappearance is not fully accounted for through the rate of formation of only CO and cyclopentadiene. However, in this case, no oxygenated products except CO have been identified and any minor species present have been explained based on cyclopentadiene pyrolysis. These results can only mean that there is another possible path for phenol decomposition; one which most likely involves the formation of benzene and water (44). Once again, this route to phenol decay cannot be verified using the experimental system since small increases in benzene concentration will be unnoticed against the high background levels, and the analysis system cannot detect the presence of  $\text{H}_2\text{O}$  in product samples. However, if the formation of benzene is indeed a major decomposition path for phenol then the implication for benzene oxidation processes is important; a large fraction of the phenol formed by O atom addition to benzene may revert to benzene and thus not contribute to benzene consumption.

The conclusions that have been obtained from this aspect of the study are:



1. The decomposition of phenol can be observed on the time scales available in the turbulent flow reactor. Examination of the decomposition products suggests that there are two major pyrolysis routes: a) definitely, decomposition to CO and cyclopentadiene, b) decay to benzene and water.

2. The true order of phenol pyrolysis is close to unity and the half-life is approximately 0.3 sec.

3. Cyclopentadiene pyrolysis products similar to those suggested by other investigators (42,43) were identified.

4. Pure phenol should be melted and pyrolysed (without the benzene carrier) in order to verify benzene formation from both the phenol and cyclopentadiene pyrolysis pathways. In addition, water formation should be monitored throughout the reaction.

#### E) Construction of the Phenol Melter

It was apparent from the results of the phenol pyrolysis experiments described above, that a pyrolysis experiment without the presence of benzene carrier was necessary. One element of the work that a Ph.D. student conducted had been the design and construction of a phenol melter. Such a melter permits the flow reactor examination of pure phenol. The melter was begun with support under this program. The melter was completed and results obtained from it with support from the Department of Energy only after NASA support was terminated. Therefore, only a schematic, Figure 14, and a description of the melter will be presented here.

The equipment operates by heating a reservoir of phenol crystal to 70°C where it is melted. The liquid phenol is displaced into an evaporator by a metered flow of water. Water is separated from phenol by a stainless steel piston. The evaporator temperature was maintained at 250°C.

The reservoir consists of two separate stainless steel cylinders, with internal volumes of 375 cubic centimeters each. The metered flow of water is heated to keep the piston/cylinder assembly isothermal and enters the bottom of both cylinders in parallel. The phenol is displaced from the top. Liquid phenol leaving the cylinders is carried by heated lines to the evaporator. The entire assembly is contained in a portable Captair fume hood as a precaution against the release of toxic phenol vapor.

Within this melter/evaporator, phenol only comes in contact with stainless steel, teflon, or viton seals. The mass flow rate of phenol into the flow reactor was calculated from the metered volume flow of water into the melter/evaporator and the temperature/density properties of liquid phenol and water. The phenol was supplied by EM Science as 99%+ pure and stabilized with 0.15% hypophorous acid. The stabilizer is not expected to have an effect since for a fuel concentration of 2000 ppm, there will be only 3 ppm of hypophorous acid in the gas phase. Hydrocarbon impurities were less than 0.06% by gas chromatographic analysis.

Phenol, like most highly polar organic compounds, is difficult to analyze. For this work, the best separations and quantifications were obtained with a wide bore capillary column on a Hewlett Packard 5840 gas chromatograph. The column is 30 meters long with an inside diameter of 0.53 millimeters and a liquid phase film thickness of 2.65 micrometers. The liquid phase is crosslinked methyl silicone gum.

#### Summary

A series of flow reactor experiments aimed at understanding the role played by O atom addition to the aromatic ring during the oxidation of benzene and toluene have been conducted. Though this NASA program was terminated

before a complete understanding of pertinent O atom chemistry was achieved, a number of useful insights were obtained from the series of experiments and have been described in the preceding report. The basic focus of this work is currently being continued through the Department of Energy support.

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Supported Research

- 1). "Phenol Pyrolysis", Eastern States Section Meeting/Combustion Institute, Providence, Rhode Island, November 8, 1983. E. Wechman.
- 2). "The Effects of NO<sub>2</sub> Addition on the Oxidation of Toluene", Eastern States Section Meeting/Combustion Institute, Clearwater Beach, Florida, December 4, 1984. K. Brezinsky.

# BENZENE OXIDATION: PROPOSED MECHANISM

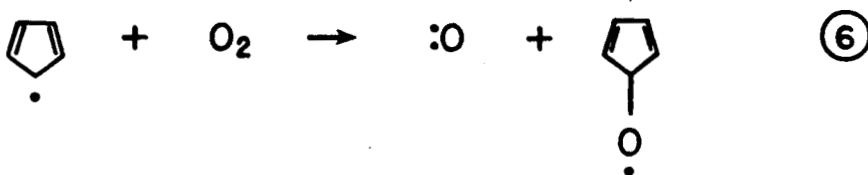
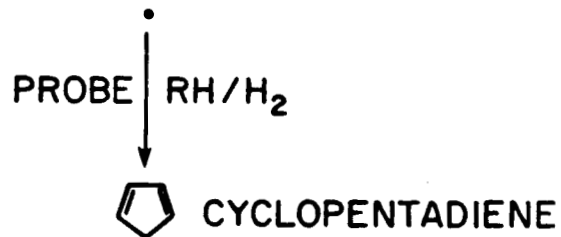
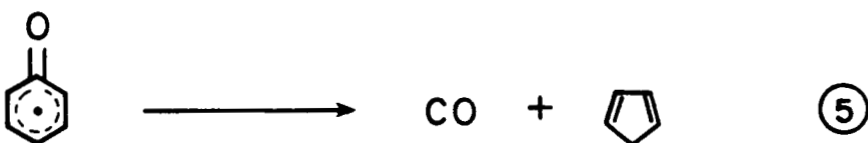
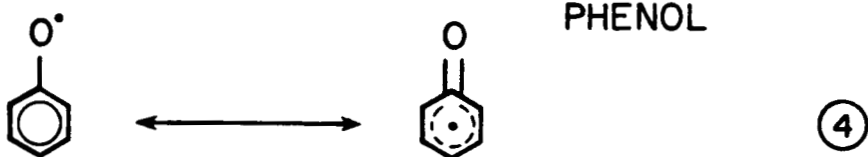
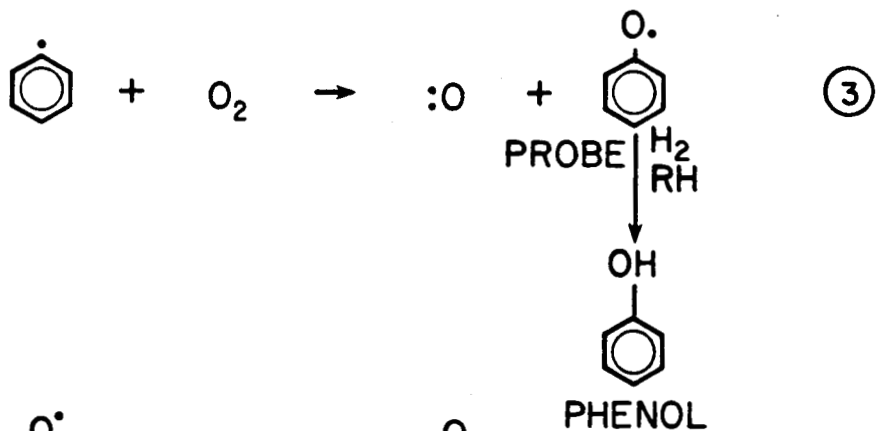


Figure 1. Benzene oxidation mechanism



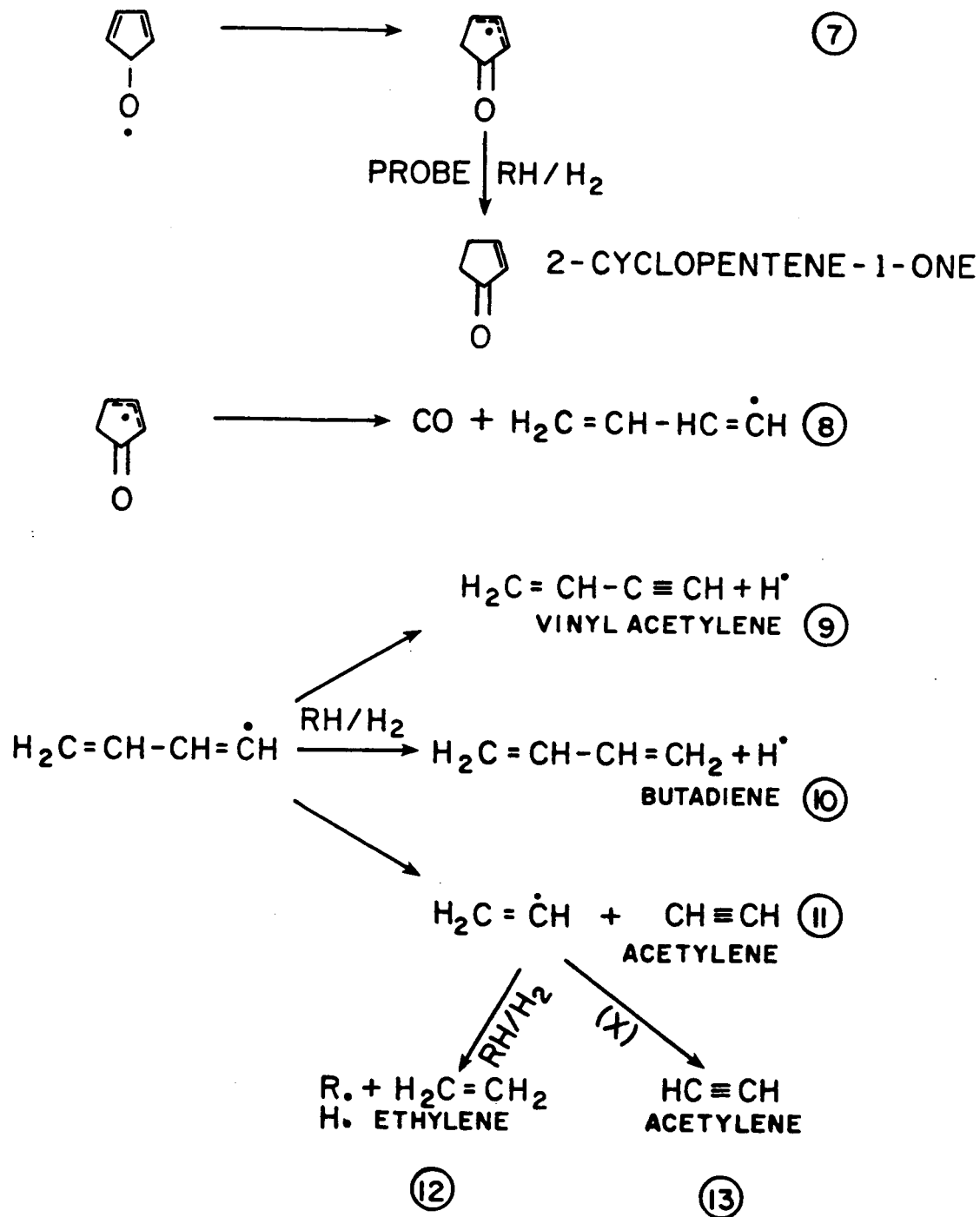
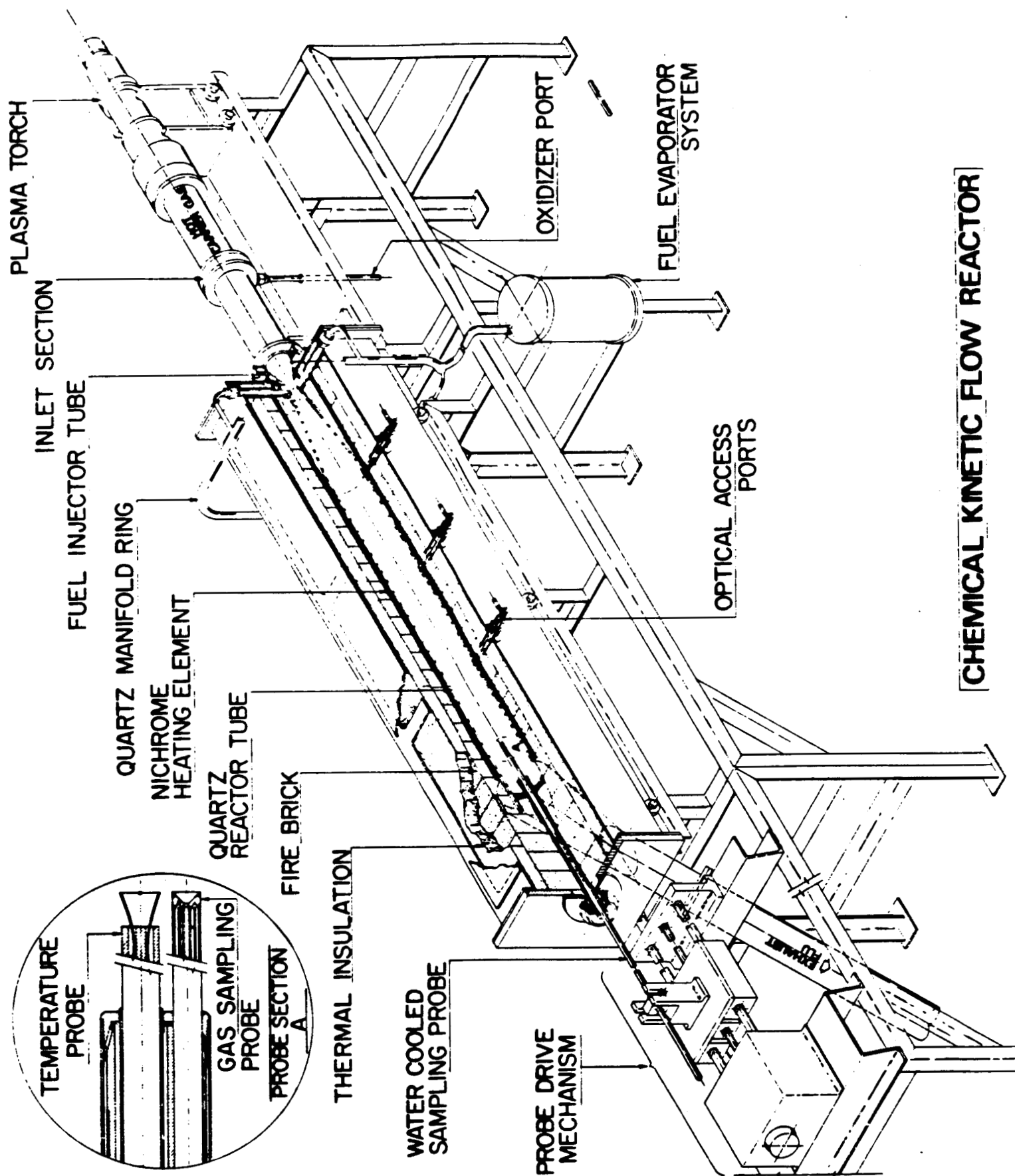


Figure 1. Benzene oxidation mechanism (continued)

Figure 2. The Princeton University high-temperature, adiabatic, turbulent plug flow, chemical kinetic reactor.



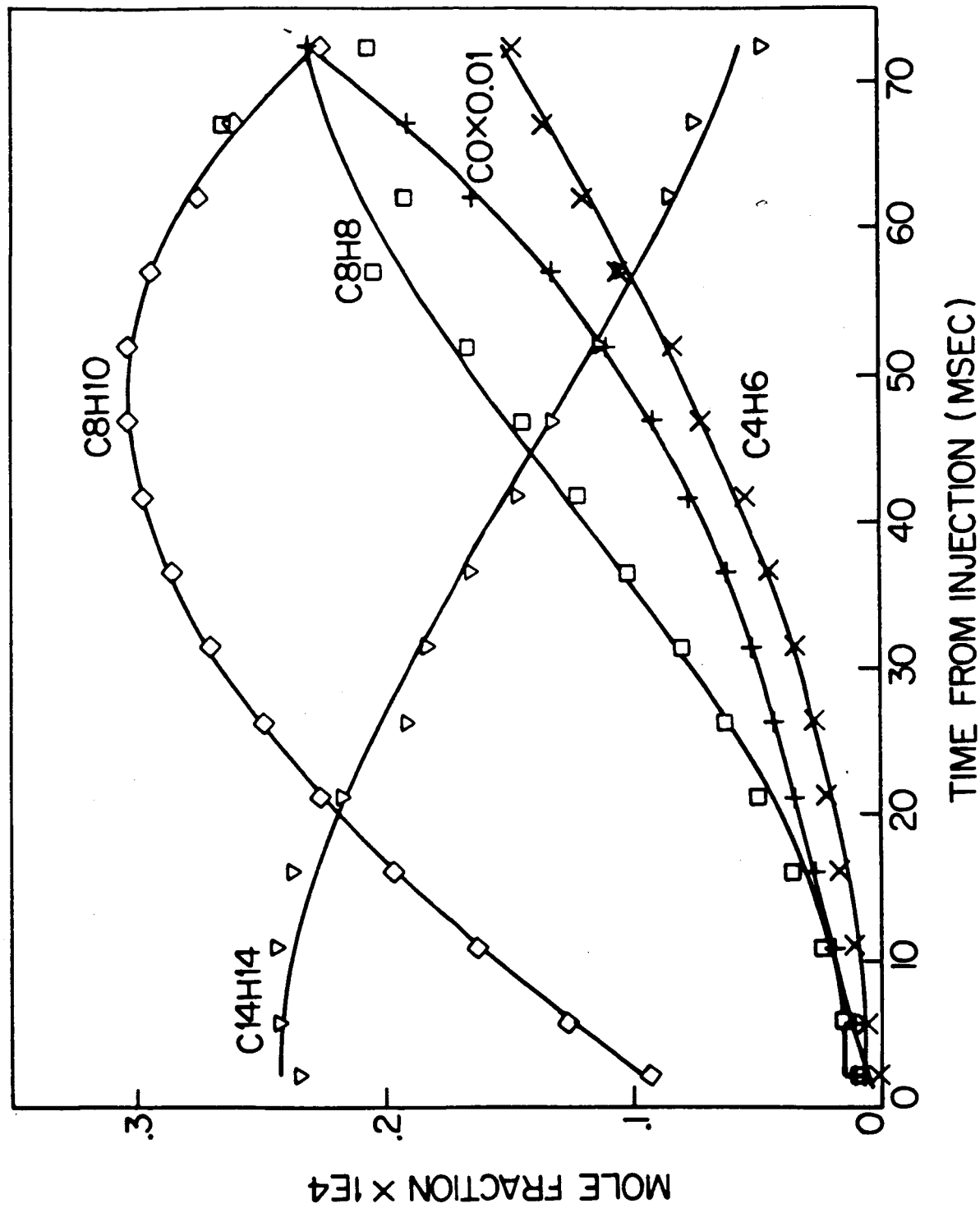


Figure 3. Dibenzyl ( $C_{14}H_{14}$ ), ethylbenzene ( $C_8H_{10}$ ), styrene ( $C_8H_8$ ), butadiene ( $C_4H_6$ ), and carbon monoxide (CO) species profiles from a fuel lean toluene oxidation ( $\phi = 0.63$ ).

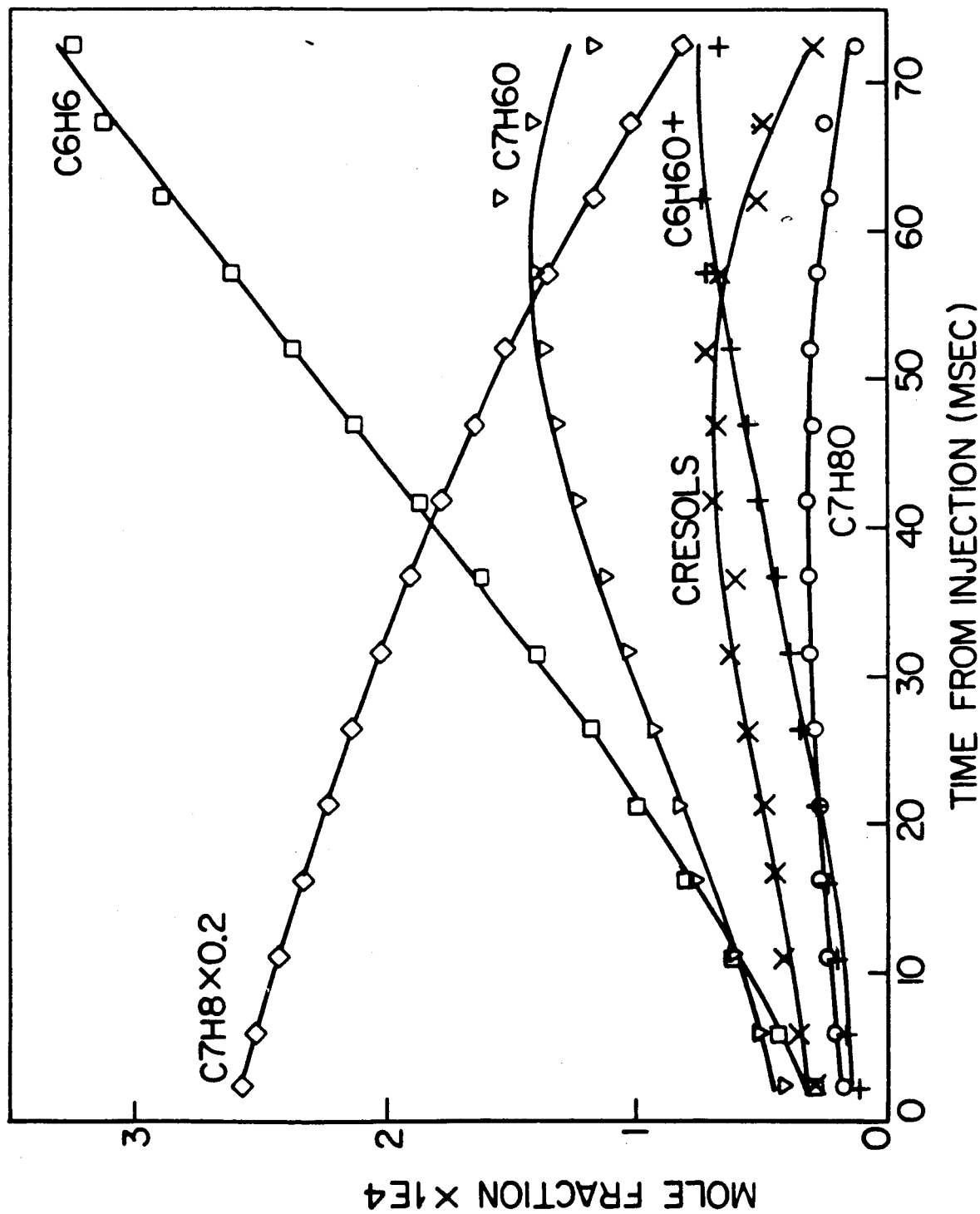


Figure 4. Species profiles of the oxygenated intermediates formed during a lean toluene oxidation ( $\phi = 0.63$ ). "Cresols" represents the total amount of ortho, meta, and para cresol ( $C_7H_8O$ ). Also shown are benzaldehyde ( $C_7H_6O$ ), benzyl alcohol ( $C_7H_8O$ ), phenol ( $C_6H_6O$ ), and for reference benzene ( $C_6H_6$ ) and toluene ( $C_7H_8$ ).

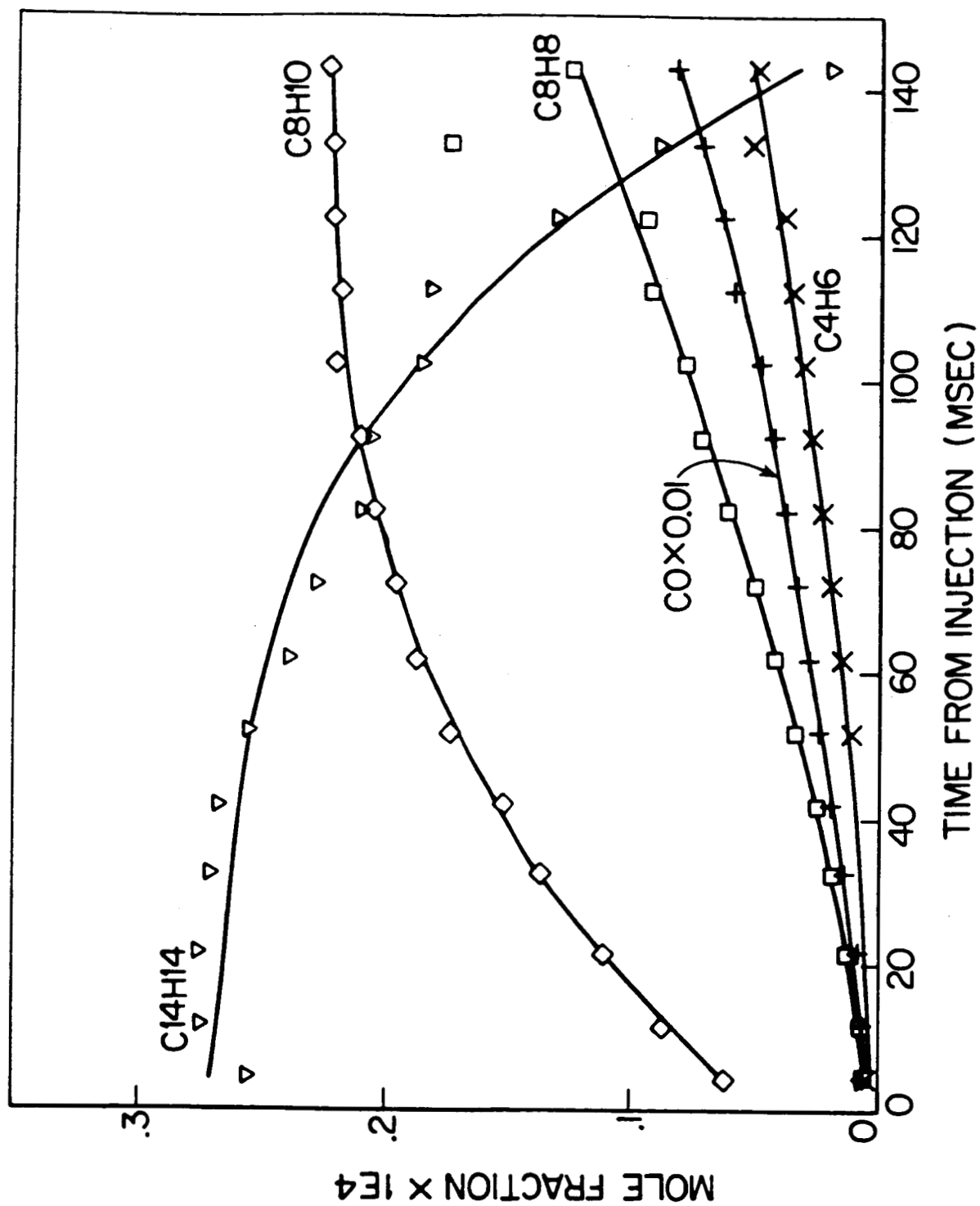


Figure 5. Dibenzyl, ethylbenzene, styrene, butadiene, and carbon monoxide species profiles from a rich toluene oxidation ( $\phi = 1.4$ ).

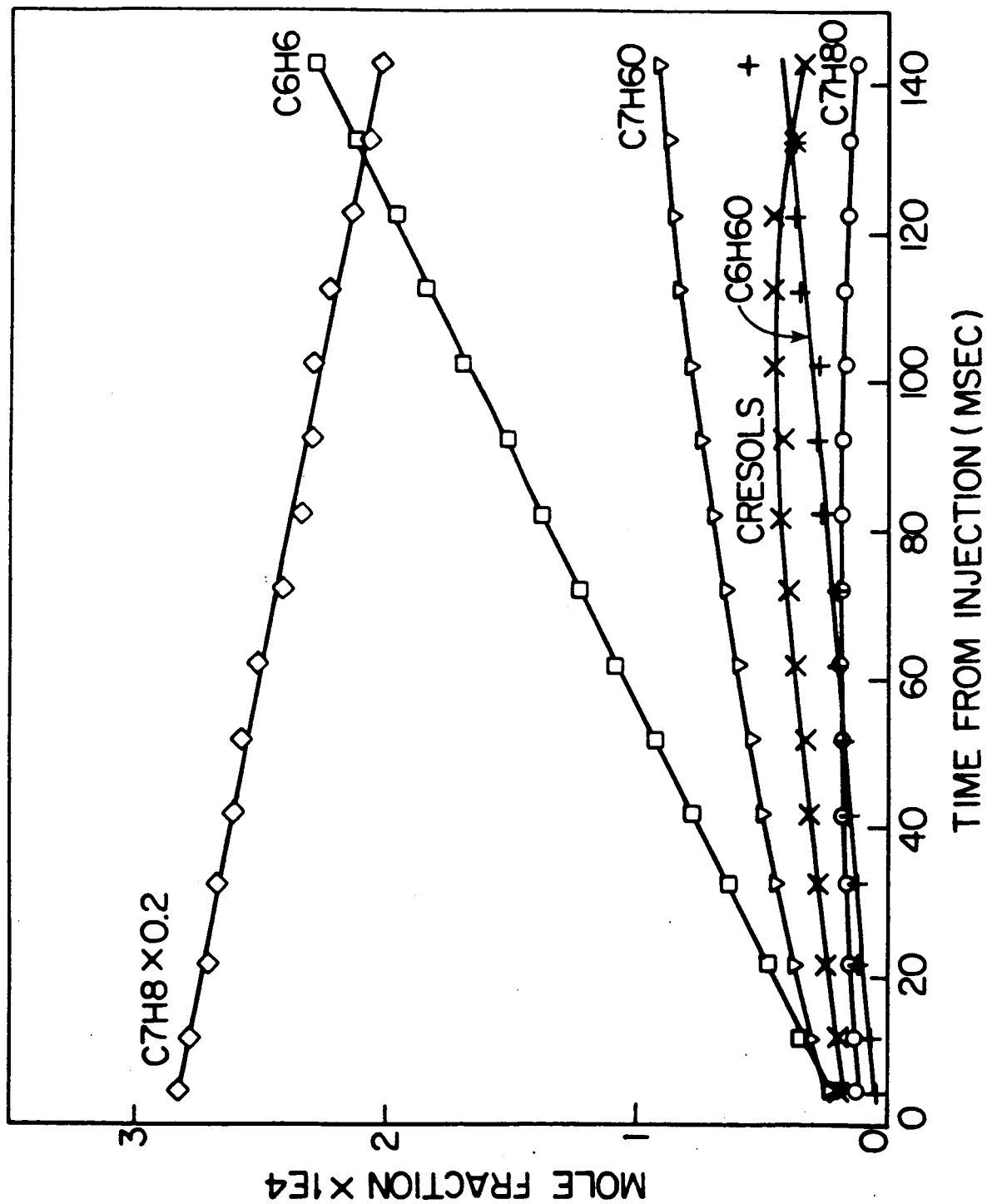


Figure 6. Species profiles of the oxygenated intermediates formed during a rich toluene oxidation ( $\phi = 1.4$ ). The same species are displayed as in Figure 5.

# EFFECT OF NO<sub>2</sub> ON TOLUENE OXIDATION

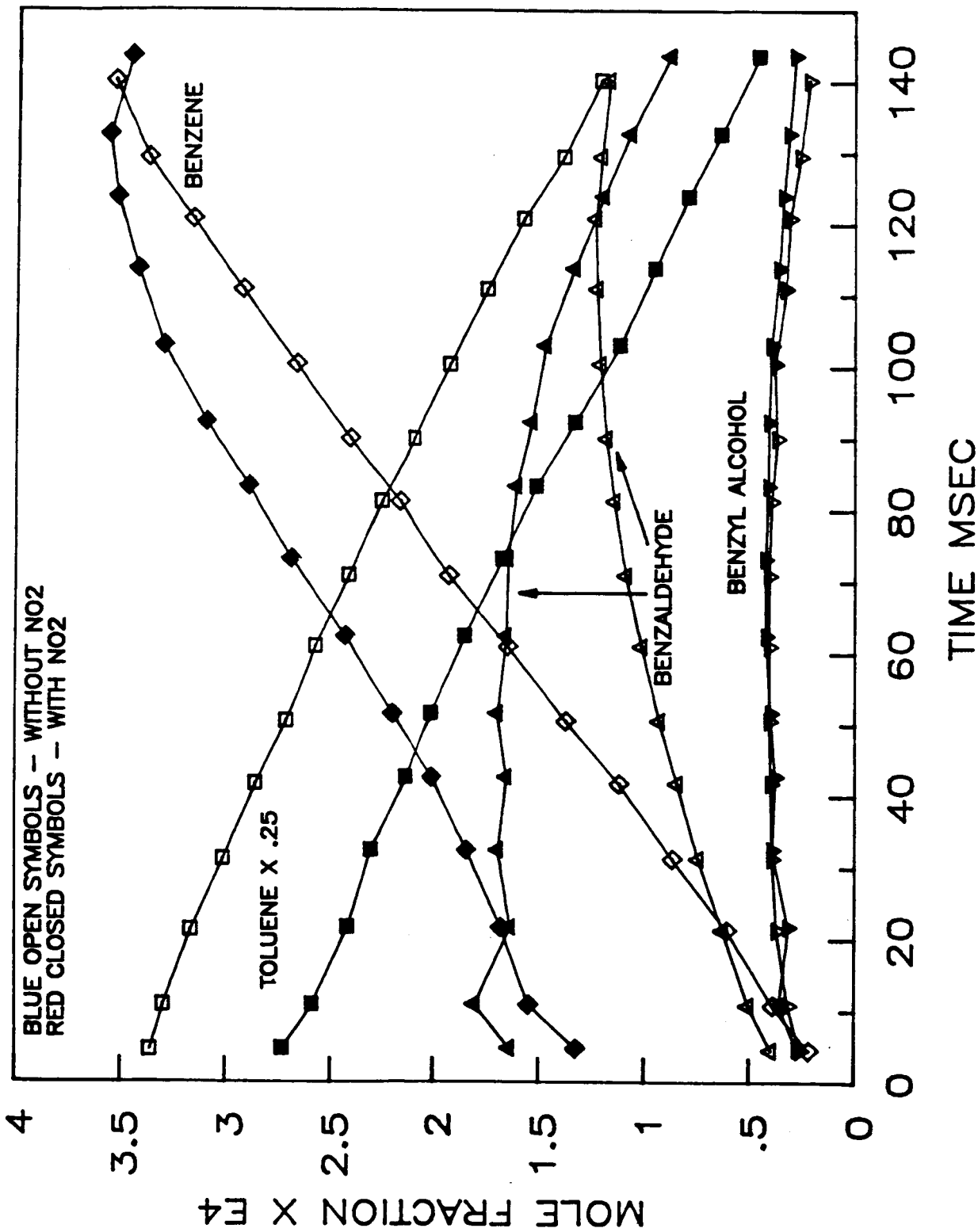


Figure 7a. Comparisons of the selected species profiles obtained from a stoichiometric toluene oxidation experiment with and without the addition of NO<sub>2</sub>.

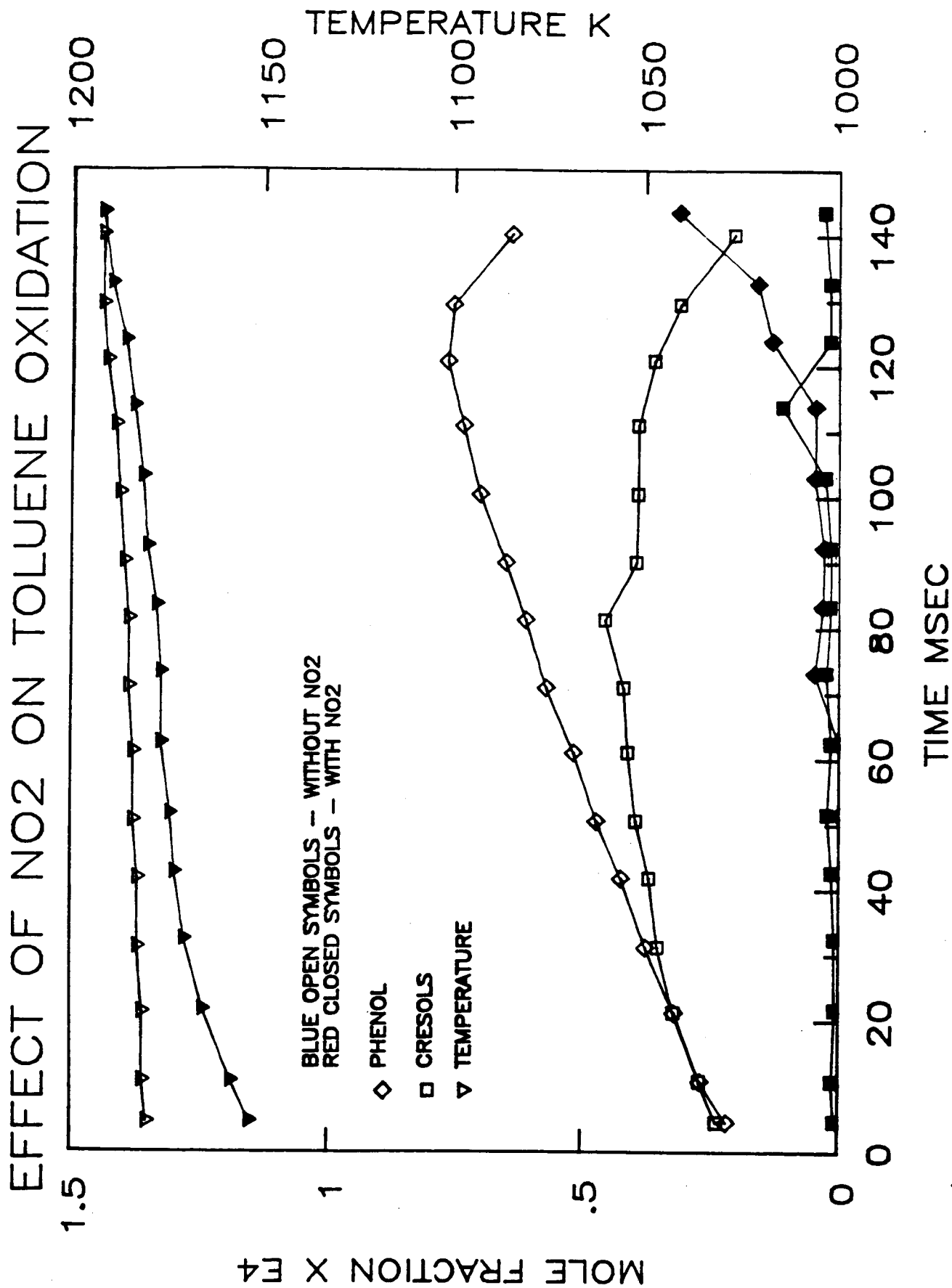


Figure 7b. Comparisons of the selected species profiles obtained from a stoichiometric toluene oxidation experiment with and without the addition of NO<sub>2</sub>.



# TOLUENE OXIDATION WITHOUT NO2

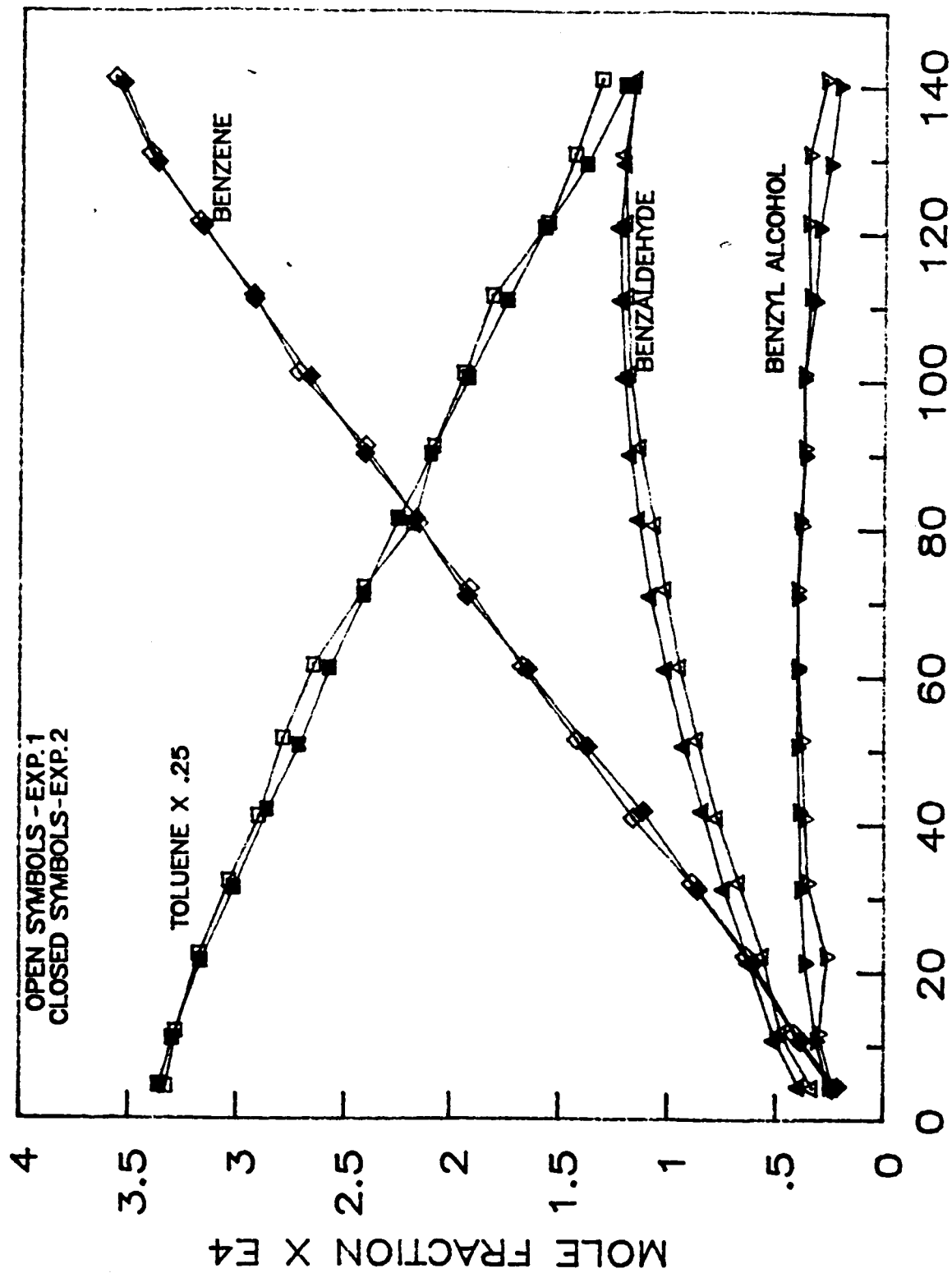


Figure 8a.

Comparisons of the selected species profiles obtained from two different stoichiometric toluene oxidation experiments.

# TOLUENE OXIDATION WITHOUT NO2

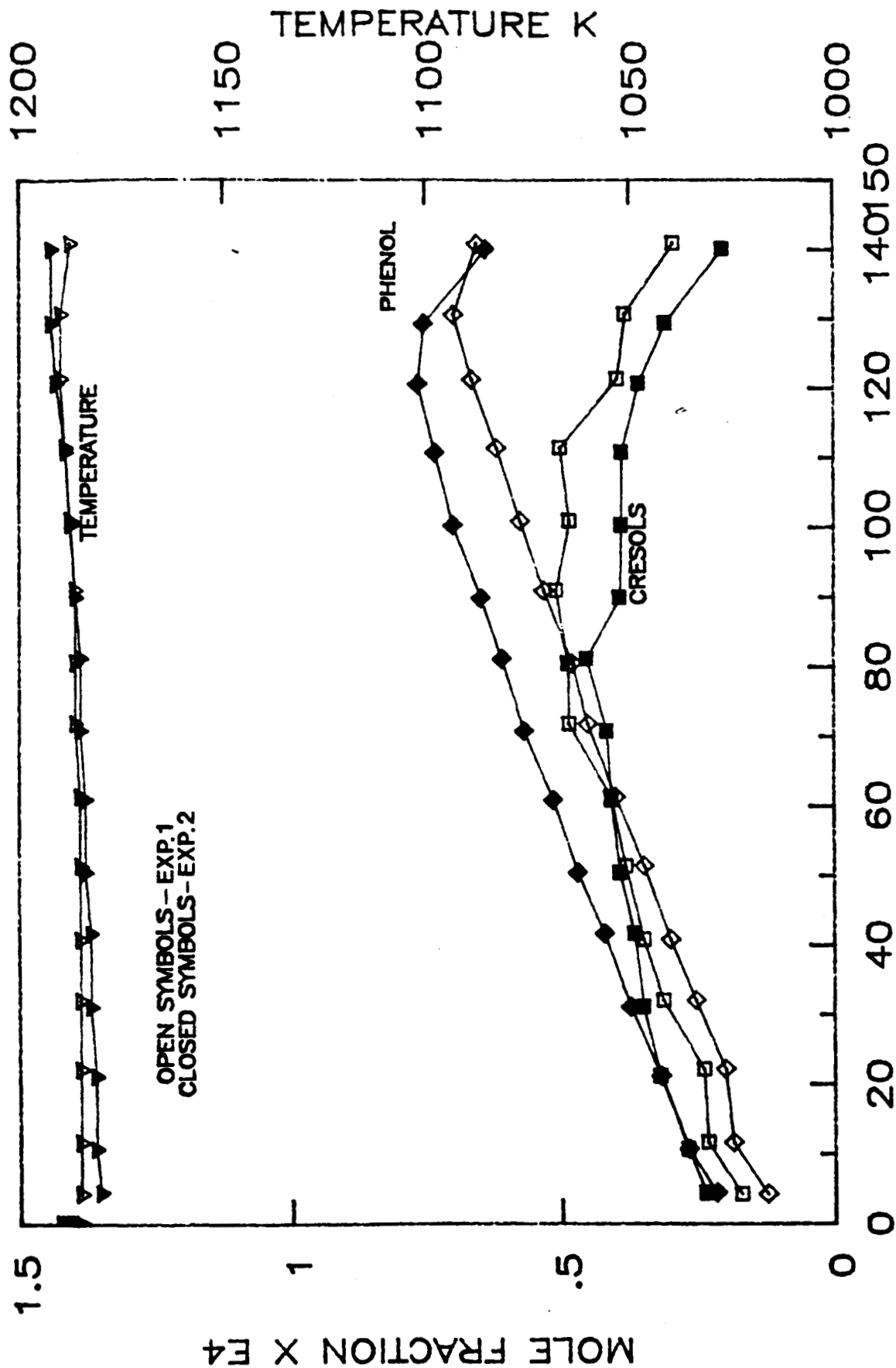


Figure 8b. Comparisons of the selected species profiles obtained from two different stoichiometric toluene oxidation experiments.

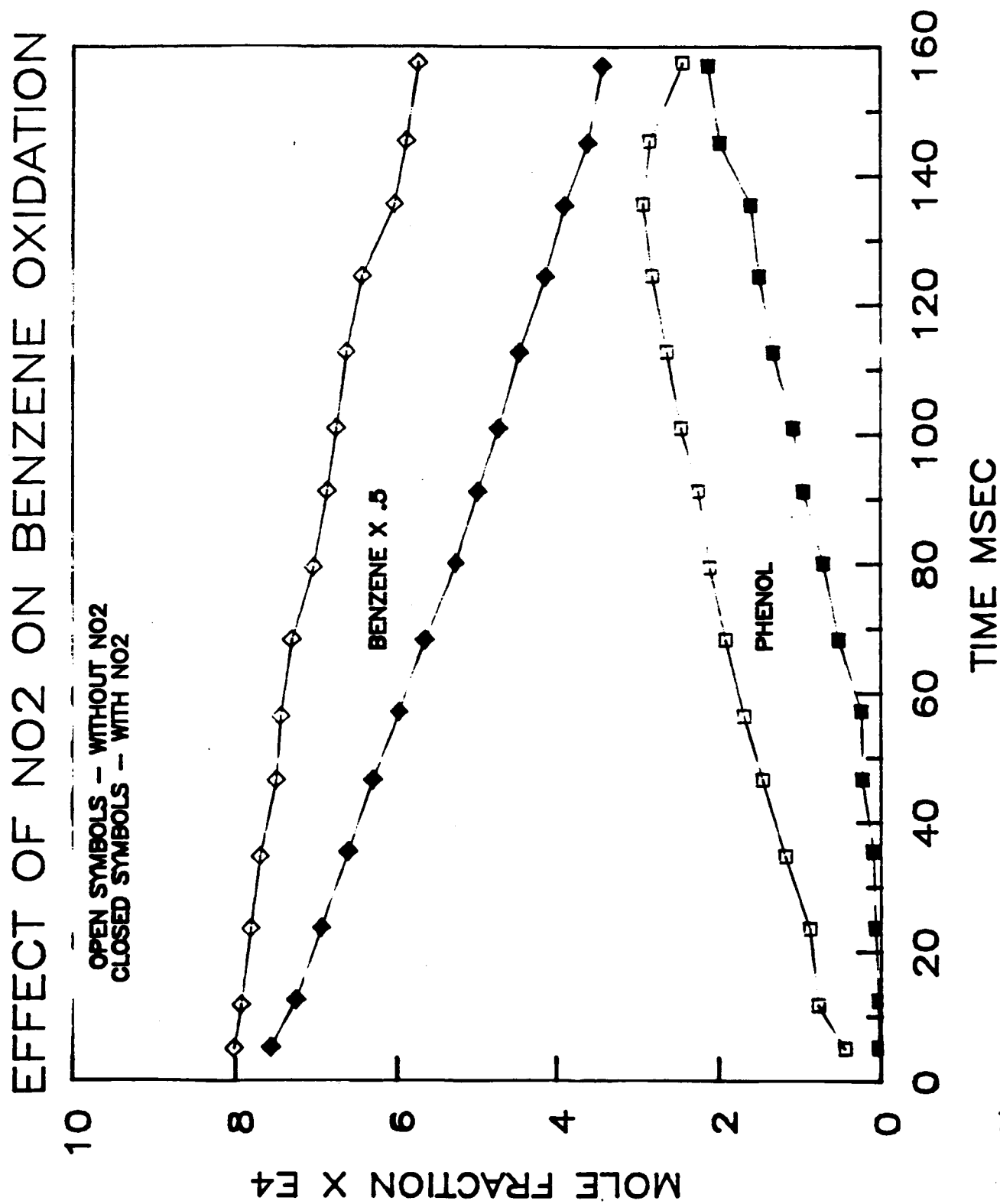


Figure 9. Comparisons of the selected species profiles from a stoichiometric benzene oxidation with and without NO<sub>2</sub>.

# EFFECT OF NO2 ON BENZENE OXIDATION

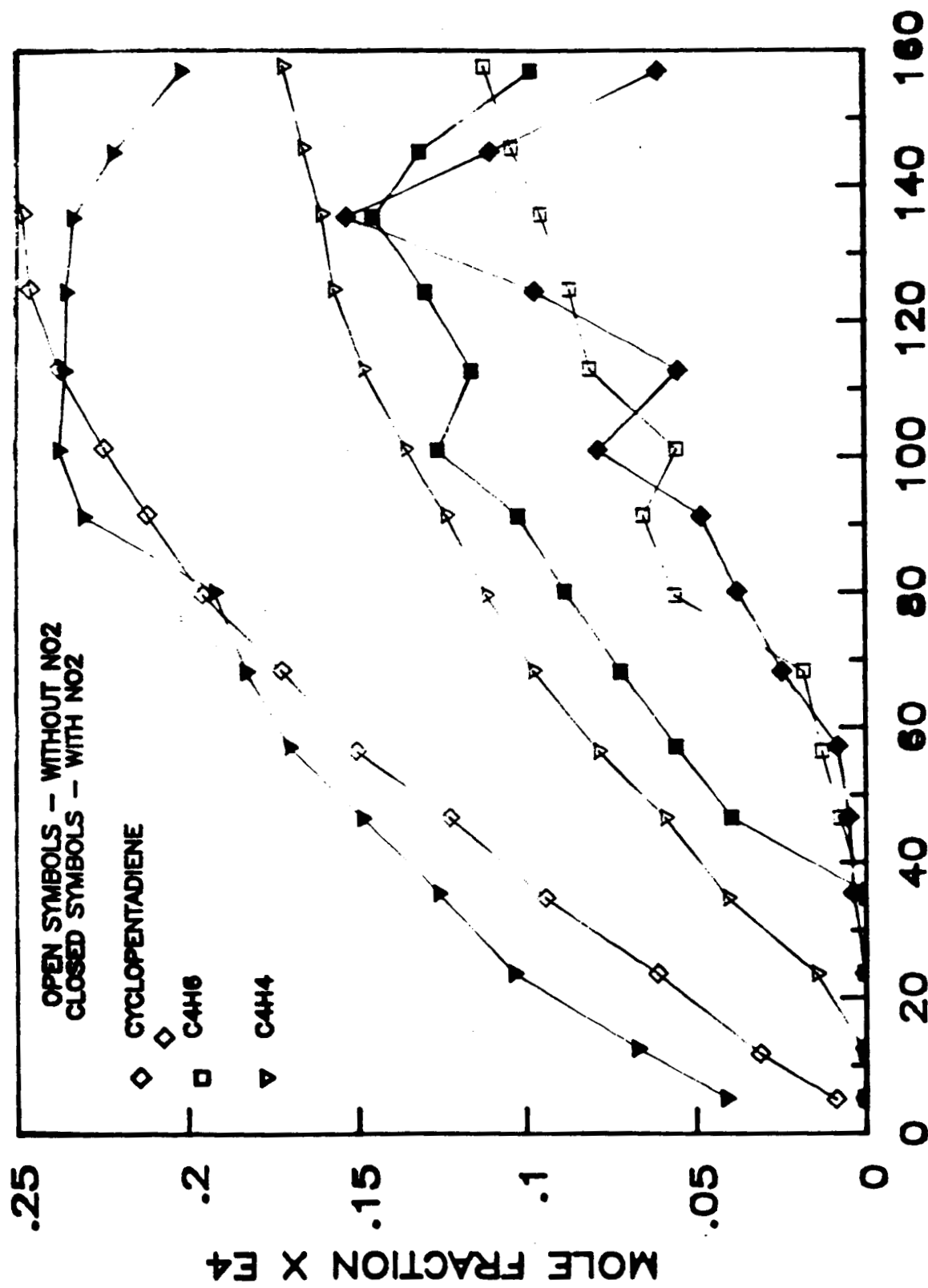


Figure 10. Comparisons of the selected species profiles from a stoichiometric benzene oxidation with and without NO<sub>2</sub>.

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Run	CO	t <sub>1</sub>	$\frac{C_1}{C_0}$	$\frac{C_1^*}{C_0^*}$	t <sub>2</sub>	$\frac{C_2}{C_0}$	$\frac{C_2^*}{C_0^*}$
12	5.00e-5	.0762	.091	.042	.1305	.794	.741
13	7.14e-5	.06364	.027	.044	.1433	.797	.719
15	5.30e-5	.0726	.025	.046	.1327	.800	.736

t<sub>0</sub> = 0.00 from intercept.  $\frac{C_1}{C_0}$  = actual C<sub>1</sub> value at t<sub>1</sub> from run data

$\frac{C_1^*}{C_0^*}$  = exp(-kt) = exp(-2.0 t<sub>1</sub>) = 0.1

TABLE 1

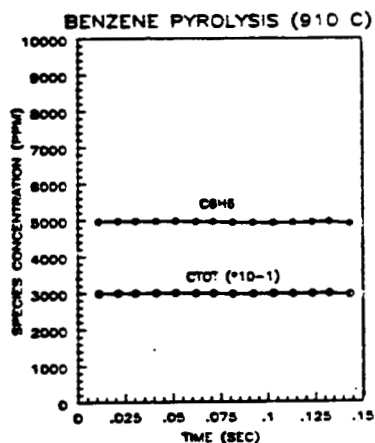


FIGURE 11

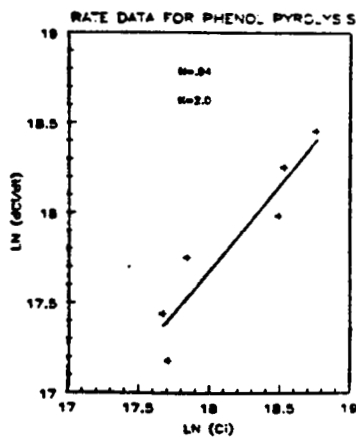


FIGURE 12

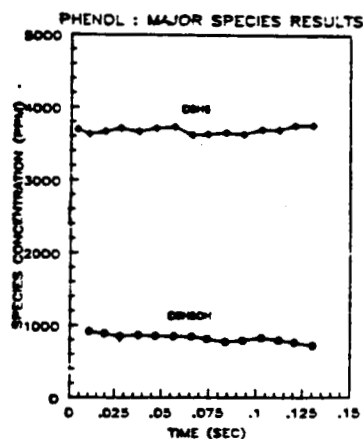


FIGURE 13a

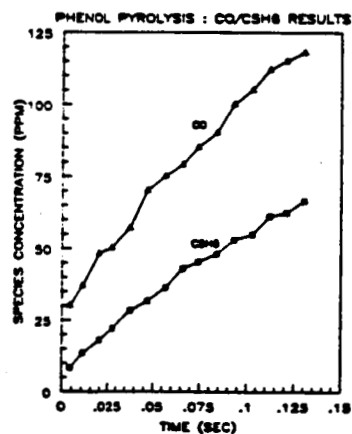


FIGURE 13b

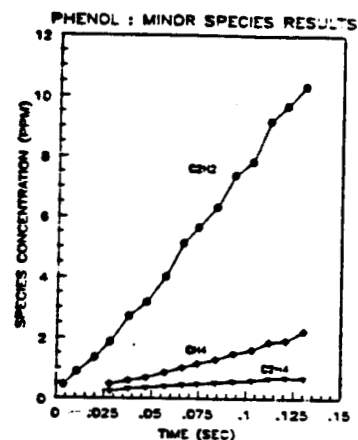


FIGURE 13c

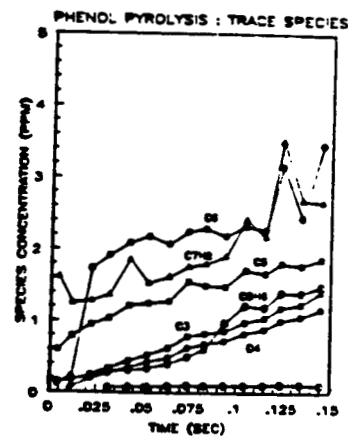


FIGURE 13d

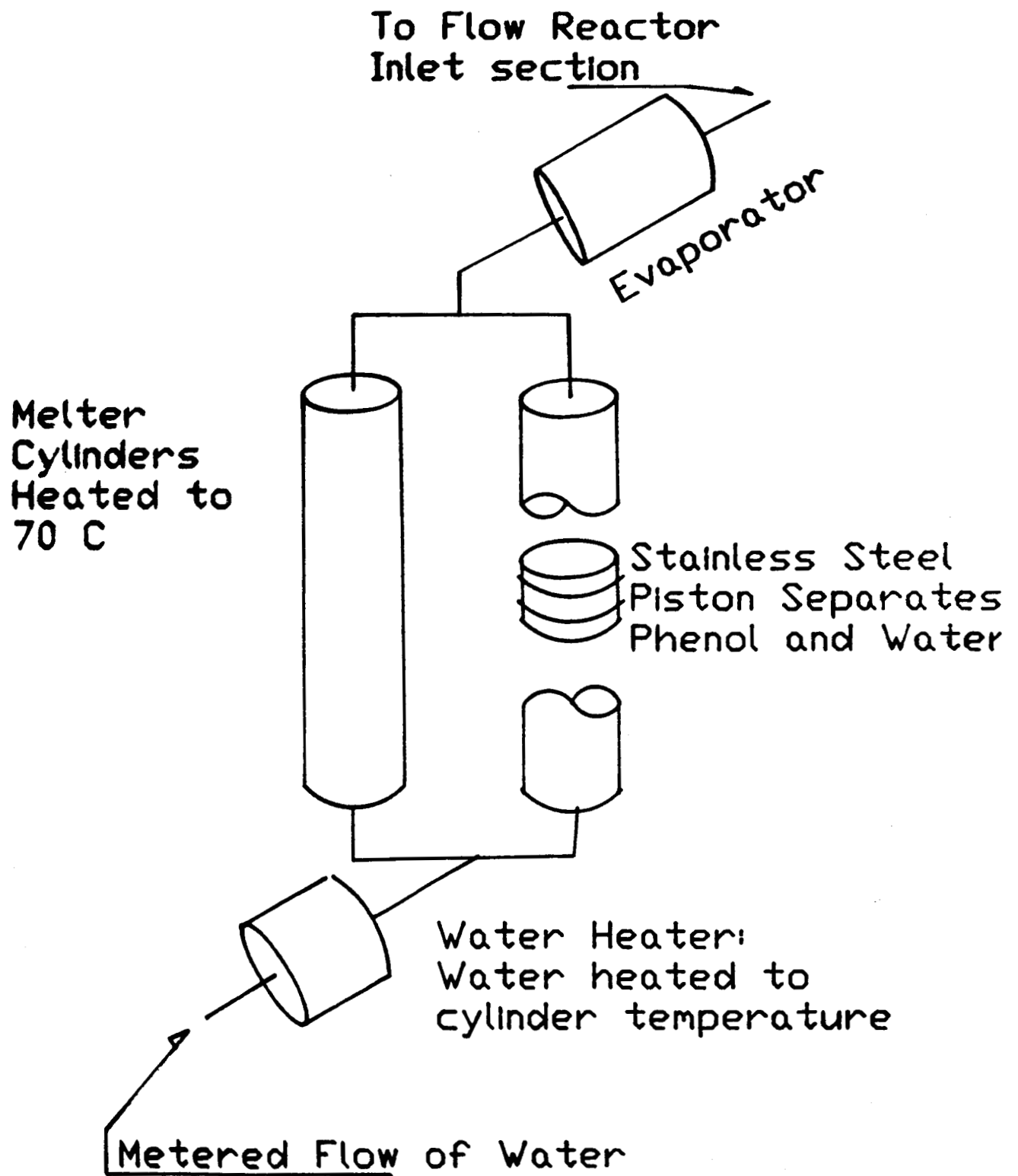


Figure 14. Schematic representation of the Phenol melter